THE CATHOLIC UNIVERSITY OF AMERICA

Washington, D. C.

Technical Report No. 2

Copy No. _38_

LUMINESCENCE PRODUCED AS A RESULT OF INTENSE

ULTRASONIC WAVES

by

Virginia Griffing

and

Daniele Sette

Contract Nonr-331(00)

Submitted by: Dr. F. O. Rice
Head of Chemistry Department
The Catholic University of America
Washington, D. C.

LUMINESCENCE PRODUCED AS A RESULT OF INTENSE ULTRASONIC WAVES*
by
Virginia Griffing and Daniele Sette**
Department of Chemistry, Catholic University of America

Abstract

The luminescence produced by intense ultrasonic waves has been
investigated in a number of water solutions and organic liquids in
the frequency range .66 – 2 Mc/s. Together with direct visual tests,
quantitative measurements have been performed for which a photometric
method has been developed. The results show that luminescence, when
it does occur, is always present with cavitation and starts at the
same energy level as cavitation. Various water solutions show
luminescence in the same relative amounts as the yield of the chemical
reaction caused by intense sound waves. From this it is concluded
that, at least in these cases, the phenomenon is chemiluminescence.
Among the organic liquid tested only nitrobenzene has shown a very
weak luminescence in the frequency range and under the physical
conditions examined. It is not possible at present to conclude
whether this weak luminescence is due to some chemical reaction
occurring in it or to a different process. An apparent frequency
dependence for the intensity of luminescence was observed; however,
it was shown that the threshold of cavitation was the frequency
dependent phenomenon.

Errata

Figures 1-5 do not appear in this report but
will appear in the final paper to be published.

1. Introduction

Many experimenters have reported the observation of luminescence produced by high intensity sound waves in liquids at different frequencies and hypotheses have been made concerning the origin of this phenomenon. All authors agree that luminescence can only be present when cavitation also occurs. L. A. Chambers[1] tested a considerable number of liquids in the low frequency range 1-5 Kc/sec. He found that the intensity of the light produced by sound increased with the product of the dipole moment and the viscosity coefficient of the liquid. The higher light intensities were observed in glycerine and nitrobenzene; the lower ones in the monohydric alcohols. Water, however, has a much larger luminescence than would be expected from its dipole moment and its viscosity.

In a higher frequency range, a few hundred kc/sec., E. N. Harvey[2] has studied numerous solutions of different substances in water and interprets his results as excluding the possibility of chemiluminescence as an explanation of the observed phenomena. In particular the fact that luminescence is present in water saturated with nitrogen led him to the conclusion that the presence of oxygen is not necessary for luminescence in water. Moreover, the great variety of conditions under which the luminescence occurs in reducing or oxidising solutions is for him an evidence of nonchemical origin of luminescence. Harvey suggests that we are dealing with electroluminescence. However, more

1. L. A. Chambers, J. Chem. Phys. 5, 230(1937)
2. E. N. Harvey, J. Am. Chem. Soc., 61, 2392(1939)

recent experiments have shown that there are chemical effects in all
cases in which Harvey observed luminescence.

J. Frenkel[3] proposed the idea that the origin of luminescence
may be due to a kind of balloelectricity. As a consequence of high
intensity sound waves, the liquid is torn apart producing cavities in
which electric charges are formed on opposite parts of the surface.
During the collapse of a bubble an electric discharge takes place
with production of light and formation of active oxygen which may be
responsible for the chemical effects observed. This theory is based
on the hypothesis that cavitation is produced by effective tearing
of the liquid and not by a gradual growing of the bubbles from nuclei.
It is difficult to accept this hypothesis because cavitation and
luminescence may be observed with intensities of the sound waves far
below the ones that would be required to overcome the inter-molecular
forces.

Recently E. A. Neppiras and B. E. Noltingk[4] have studied
solutions of carbon tetrachloride in water in the frequency range
500 Kc/sec - 2 Mc/s and propose as alternative explanation of
luminescence the possibility that the temperature inside the bubbles
increases during their collapse so much as to produce incandescence
of the gases inside.

3. J. Frenkel, Acta Physicoch. 12, 317(1940)
4. E. A. Neppiras, B. E. Noltingk, Mullard Res. Lab. Report 135(1951)

In previous investigations the hypothesis was made[5] and tested[6,7] that cavitation bubbles act + as hot spots which are responsible for chemical reactions, as also suggested by Neppiras and Noltingk.

It was found that such reactions occur only within the bubble and depend on the gas in the bubble. Aqueous solutions of carbon totrachloride give free chlorine if the gas is A or CO, not if it is H_2. In ether, acetone, methylalcohol, benzene and nitrobenzene saturated with air, no chemical effects are found.

From this brief survey it appears that the origin of the sonoluminescence is not yet clearly understood and that it is necessary to gather more experimental data. The experimental study of these phenomena is made difficult because the observed light intensity is very low. Thus, up to now the observations have been of a qualitative nature.

For these reasons we have made some experiments to clarify the nature of the phenomena and have developed an experimental set-up for quantitative measurements on luminescence to further explain previous data[8] obtained from direct visual observations.

5. V. Griffing, J. Chem. Phys. 18, 997(1950)
6. H. E. Fitzgerald, The Role of Dissolved Gases in Chemical Reactions produced by Ultrasonics, Ph. D. Thesis, Catholic University of America Press (1951).
7. V. Griffing, J. Chem. Phys. 20, 939(1952)
8. V. Griffing-D. Sette-Phys. Rev. 87,234(1952)

2. Apparatus and methods of measurement

For direct visual observations a simple experimental arrangement was used. A quartz crystal mounted in a holder described below has been used for generating sound waves which are transmitted through a layer of water to the liquid contained in the test tube. The open end of the tube was closed by a thin sheet of nylon which permitted 99% of the sound energy to enter the liquid. The observations were made in a dark room after the eyes became accomodated to the low intensity light.

In the arrangement described the layer of water between quartz and test tube becomes luminescent. This is not a great inconvenience if the liquid in the tube is strongly luminescent, because the eyes distinguish the different luminous places, but is troublesome if the second liquid is scarcely luminescent or not luminescent at all. In these cases we have used as intermediate liquid ether or a mixture of water and ether where no luminescence was found.

The experimental set-up used for quantitative measurements of luminescence is shown in the block diagram of figure_3. The liquid is contained in a small chamber in which one wall was a quartz crystal for generating sound waves and the opposite wall was a glass window. The photosensitive tube was located on the back of the window. This tube was a RCA 931 A and it is a part of a photo-multiplier microphotometer (Am. Instr. Co. Type N 10-210) in which

an amplifier and a bridge circuit are designed to allow measurements
of very weak luminous flux (of the order of micromicrolumen).

An important point in the constructions of such apparatus is to
avoid any discharge between the quartz electrodes and to limit as much
as possible corona effects on the electrodes particularly inasmuch as
the voltages applied to the quartz ranged up to 3500 volts. For
these reasons the quartz is put between two circular electrodes of
diameter smaller than the quartz disc and only the central parts of
its faces are gold-plated. The electrodes moreover have been shaped
to decrease the voltage gradient. Notwithstanding these precautions
a corona effect was still detectable (especially at 1 mc/sec) with
the microphotometer at its maximum sensitivity.

In order to control the temperature, a refrigeration coil was
put around the liquid chamber and tap water was used as the circu-
lating liquid. This system was found satisfactory for our purpose,
because we intended to investigate only at room temperature and it
was necessary to change the liquid specimen very frequently for other
reasons. Cavitation produces a rapid degassing of the small quantity
of liquid in the chamber and a consequent change in its behavior.
Moreover when carbon tetrachloride was present in aqueous solutions,
the chemical reactions produce a change in the optical properties of
the liquid, with the appearance of a white cloudiness. The temperature
of the liquid when introduced in the chamber and when it was taken

away was checked and usually a temperature increase from 21 to 26° C. was obtained.

Two threaded holes have been placed in the chamber through which the liquid is passed. Two small pipes can be screwed in the holes which makes it possible to fill and empty the cell. The chamber is afterwards sealed with two screws. When water solutions saturated with gases different from air had to be tested the following procedure was used for introducing them in the ultrasonic cell: (1) the chamber is filled with distilled water; (2) the water is pushed out of the chamber by the same gas under pressure which is dissolved in the liquid to be next used; (3) the chamber is filled with the water solution from a flask where the liquid is put under a pressure higher than atmospheric.

A cylindrical shape of the liquid chamber has been chosen having the glass window parallel to the quartz. This was done to observe the light from the best position and increase the sound energy density in the liquid by reflections. This has the disadvantage that the presence of standing waves makes it difficult to specify the energy level inside the chamber. Because it has been observed that the real distribution of the sound pressures under these conditions is strongly dependent on the geometrical shape of the vessel, we have preferred to adopt a procedure developed in other cavitation threshold experiments at this university[9].

9. F. E. Fox and W. Connolly - Experimental Studies of the Cavitation Threshold in Liquids. To be published.

The method involves two assumptions: (a) that the sound intensity level at which cavitation begins is independent of the geometry of the sound field, (b) that the energy in a given sound field is proportional to V^2, where V is the voltage applied to the sound source at a given, constant frequency. Thus one determines K_1 in the relation $J = K_1 V^2$ by simultaneous measurements of the voltages and the sound intensity in a progressive, nearly plane wave system using a radiation pressure detector and fresh tap water. In the same system one determines J_{th}, the intensity level for the onset of cavitation. Using the closed vessel with the standing wave system one next determines the voltage at which cavitation begins. Since one assumes that cavitation sets in at the same local intensity as in the progressive wave, this yields the value of K_2 to be used for this particular experimental arrangement as long as the frequency remains constant and the ratio of K_1 to K_2 is assumed to depend only on the geometry of the system.

Of course, after the onset of cavitation the presence of many sound scattering bubbles disturbs the sound field in both of the above systems, but one assumes that the quadratic dependence upon voltage holds for the average intensity beyond the cavitation threshold. The cavitation thresholds obtained[*] were 0.62 w/cm^2 at 660 kc; 0.90 w/cm^2 at 1 mc and 1.65 w/cm^2 at 2 mc. The conditions

[*]These values were obtained by applying intermittent voltages to the quartz, (see (9)).

for the observation of the cavitation in the chamber were not very
favorable. This observation was made by disconnecting the phototube
attachment and using the glasswindow both for transmitting a light
beam and looking at the bubble formation. Moreover it was often
difficult to start cavitation in the chamber, so that it was some-
times preferable to determine the end instead of the onset of cavita-
tion. Accordingly the study of luminescence was usually done by
applying the maximum voltage to the quarts and recording the light
meter deflections as the voltage continuously applied to the quarts
was gradually decreased. In these conditions of course cavitation
ceased for energy levels slightly lower than when the voltage at the
quarts at the onset of cavitation.

On the same sample only two or three runs were made, and the
results given below are an average of tests on many samples. As we
have mentioned before the main reasons for making so few runs on the
same sample are the degassing of the liquid produced by cavitation
and the fact that when carbon tetrachloride is present the liquid
rapidly becomes cloudy due to chemical reactions taking place in it.
In order to correct for these changes, the reading of the light meter
given in the second and third runs have been multiplied by the ratio
of the maximum readings in the first and second runs. Table 1 shows
how the average deflections for a sample have been calculated. The
average for different samples were used to obtain the values of light
given below.

TABLE I.

Calculation of average of illuminations at the phototube for a specimen of water, carbon tetrachloride, argon solution.

Voltage at the quartz (KV)	1st Run		2nd Run		2nd Run Corrected		Average	
1	33.5	10^{-8}	24.4	10^{-8}	33.5	10^{-8}	33.5	10^{-8}
1.3	27.5		19.8		27.1		27.3	
1.6	18.9		13.4		18.4		18.6	
1.3	9.5		7.0		9.6		9.55	
2.2	5.5		3.6		5.0		5.25	
2.4	1.5		0.9		1.2		1.35	

At high ultrasonic intensity we have found that the light intensity measurements reproduce quite well. At lower ultrasonic intensities, however, large variations were found among successive runs. At this intensity, the luminescence changes very rapidly with the sound intensity. Therefore small change in gas content of the liquid, nuclei present, and other conditions which influence cavitation, have here a larger effect.

It was not possible to eliminate corona effect entirely, especially at 1 kc/sec where large electric fields were used. This is of no importance when the measurement are made in strongly luminescent liquids, like the aqueous solutions examined, because the deflections on the light meter due to corona are less than .5% of those obtained for the luminescence. In other cases, however, when the luminescence is weak or it is not present at all, the occurrence of this corona effect make the observations more complicated. The method used in these cases was to make two successive runs at t'e same voltage, always with the chamber filled with the liquid. During the first one the voltage applied at the quartz had a frequency 4-500 Kc/sec different from the crystal resonance frequency. Since the off-resonance vibration is not large enough to cause cavitation the deflection at the light meter in this case is due to the corona. The second run was made with the quartz vibrating and the cavitation going on.

For the preparation of the liquid solution, we have followed the system described by Fitzgerald[6]. Double distilled water was boiled in a flask for half an hour; after cooling, carbon tetrachloride and a desired gas are admitted in the flask to saturate the water.

The average illumination produced on the phototube sensitive surface, has been taken to characterize the luminescence produced in the liquids by sound waves. The light meter deflections therefore, have been converted to illuminations expressed in lumens/cm^2, (phots.) using another less sensitive photometer for calibration.

3. Results

A certain number of introductory observations were made with the light meter to establish the relation between luminescence and cavitation in the liquids where luminescence occurs; it has been found that in these cases the two phenomena are always together: every time cavitation was present it was also possible to observe luminescence and vice versa.

A study of luminescence in some aqueous solutions has been made at 1 Mc/sec. Figure 6 shows the results obtained in tap water and in distilled water solutions of carbon tetrachloride saturated with argon and with carbon monoxide. In figure 6 there is also a point showing the results of a series of measurements in tap water saturated with carbon tetrachloride. In this case the liquid became

Fig. 6
Luminescence in water solutions as function
of sound intensity. Frequency: 1 Mc/s
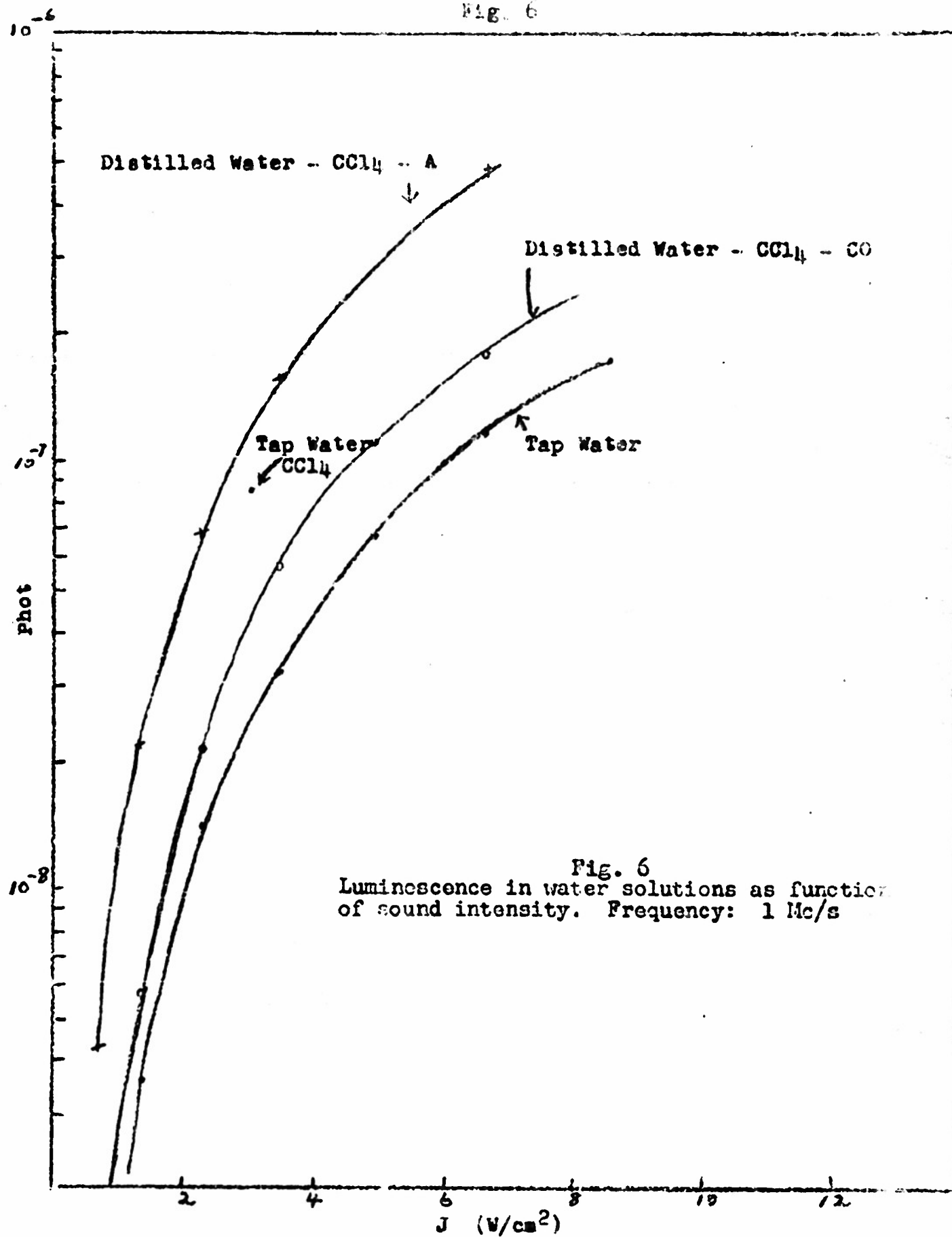
cloudy very quickly and the readings were not reproducible except
for the first deflection of the light meter at the time the cavitation
started. It is evident that the addition of air increases the
luminescence together with the chemical effects. Two other solutions
where carbon tetrachloride is present with argon or carbon monoxide
were chosen in order to compare the luminescence with the chemical
effects. The latter were found to be larger when argon is in
solution than when CO is present[6]. This is true also of the lumin-
escence.

Qualitative observations were made in other aqueous solutions
by means of visual observations, checking at the same time the
presence of chemical effects. The chemical effects were measured
by the quantitative determination of the production of hydrogen
peroxide or free chlorine by titration with potassium iodide and
sodium thiosulphate and by the measurement of the pH of the solution
before and after the sound irradiation.

It was in this way possible to see that luminescence and
chemical effects are both present in distilled water saturated,
with carbon tetrachloride and one of the following gases: oxygen,
nitrogen, sulphur, hexaflu ide. When instead, hydrogen is added
to distilled water and carbon tetrachloride, luminescence and
chemical effects disappear even though the liquid is cavitating.
It was necessary in this case to carefully remove all traces of
oxygen from the water and the hydrogen gas. For this reason the

normal method of preparing the solutions used before was modified.
Boiled triple-distilled water was frozen in a closed system which
was then evacuated. This process was repeated two times before
admitting hydrogen to the flask over a tube filled with hot copper
wire.

Some observations were made also on the following organic
liquids saturated with air: ether, acetone, methylalcohol,
benzene and nitrobenzene. The direct visual test were negative
for all of them including nitrobenzene although cavitation was
present. The measurement with the photometer gave a different
result in the case of nitrobenzene. For this measurements it
was necessary to use the photometer at its maximum sensitivity
so that it is important to take into account the deflections due
to the corona discussed above. Figure 7 gives the light at the
photometer as function of the voltage applied to the transducer
when the cavitation is present in benzene and when the quartz is
driven out of resonance. The illuminations on the phototube for
the same voltage are equal in two the cases and evidently no lumin-
escence is present. The same result is valid for ether, acetone,
and methylalcohol. Figure 8 shows the results of the photometer
measurements for nitrobenzene, where a definite difference is
present between the two curves; thus a very weak luminescence is
present. One can judge the intensity of the luminescence in this
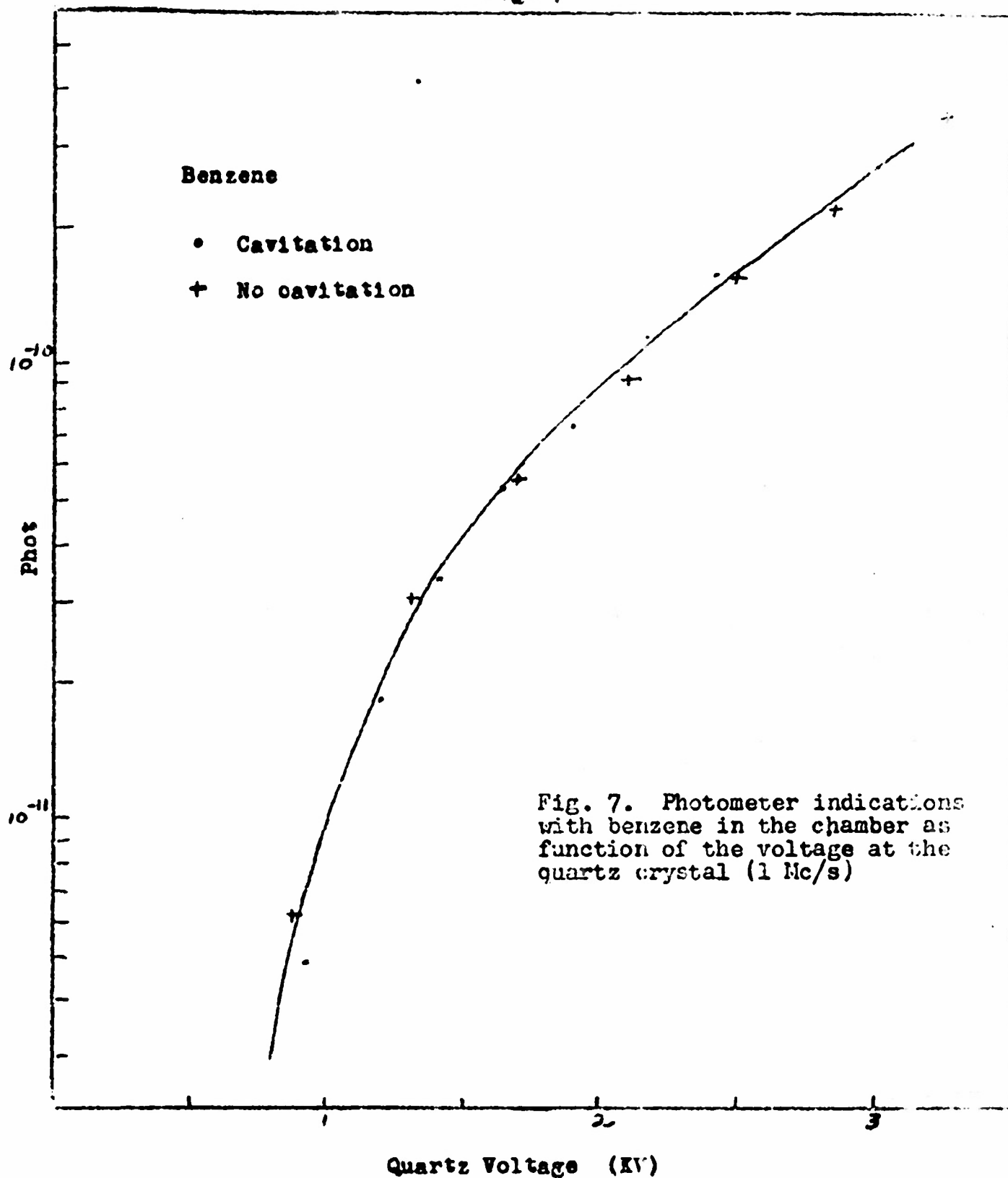case, by comparison with that in tap water; the deflections for tap

Fig. 7

Fig. 7. Photometer indications with benzene in the chamber as function of the voltage at the quartz crystal (1 Mc/s)
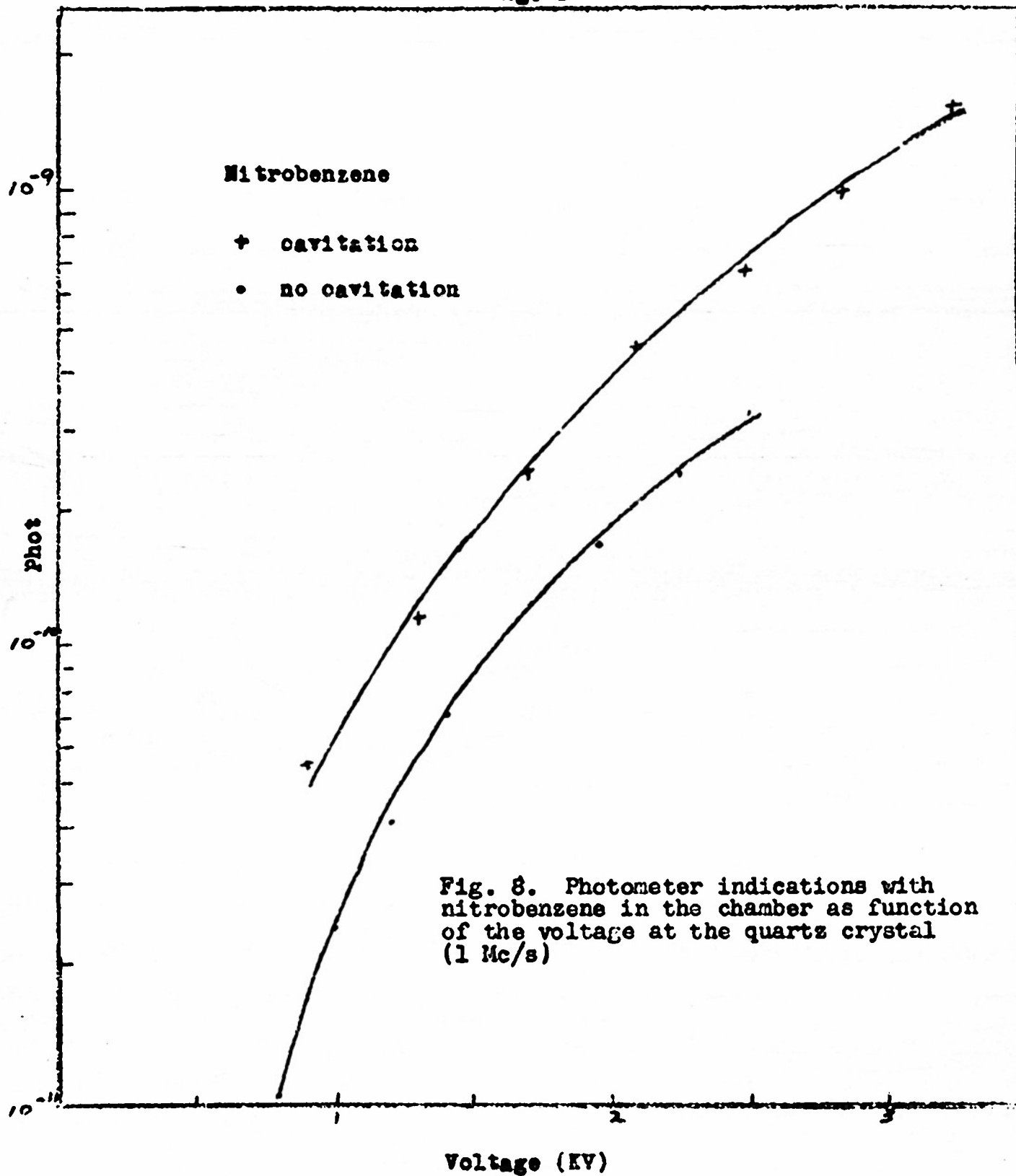
Fig. 8

Nitrobenzene

+ cavitation

• no cavitation

Fig. 8. Photometer indications with nitrobenzene in the chamber as function of the voltage at the quartz crystal (1 Mc/s)

Voltage (KV)

water at the same voltage are over 100 times larger.

The luminescence in tap water was also studied at the frequencies of 660 Kc/sec and 2 Kc/sec in order to make a comparison of the phenomena at different frequencies. The figure 9 gives the results for these two frequencies together with the ones given above at 1 Mc/sec. A source of possible error in the relative positions of the three curves is in the determination of the voltage for which cavitation starts in the liquid chamber which effects the intensity scale. The difficulties for this determination have been mentioned before. We estimate that the accuracy of the voltage determination at the cavitation threshold in the chamber is around 10% which means that the accuracy with which the intensities, as defined before are known as 15-20%. Another comparison of the results at different frequencies has been made. In figure 10 the illumination at the phototube is plotted as function of the ratio J/J_0 where J is the ultrasonic intensity and J_0 is the cavitation threshold for the respective frequencies given in figure 9. Within the accuracy of the sound intensity measurements these all lie on the same curve indicating that the apparent frequency dependence of the luminescence is actually due to the frequency dependence of the threshold of cavitation.

Discussion

These experiments have shown that when luminescence is observed

Fig. 9. Luminescence in tap water as function of sound intensity at various frequencies.
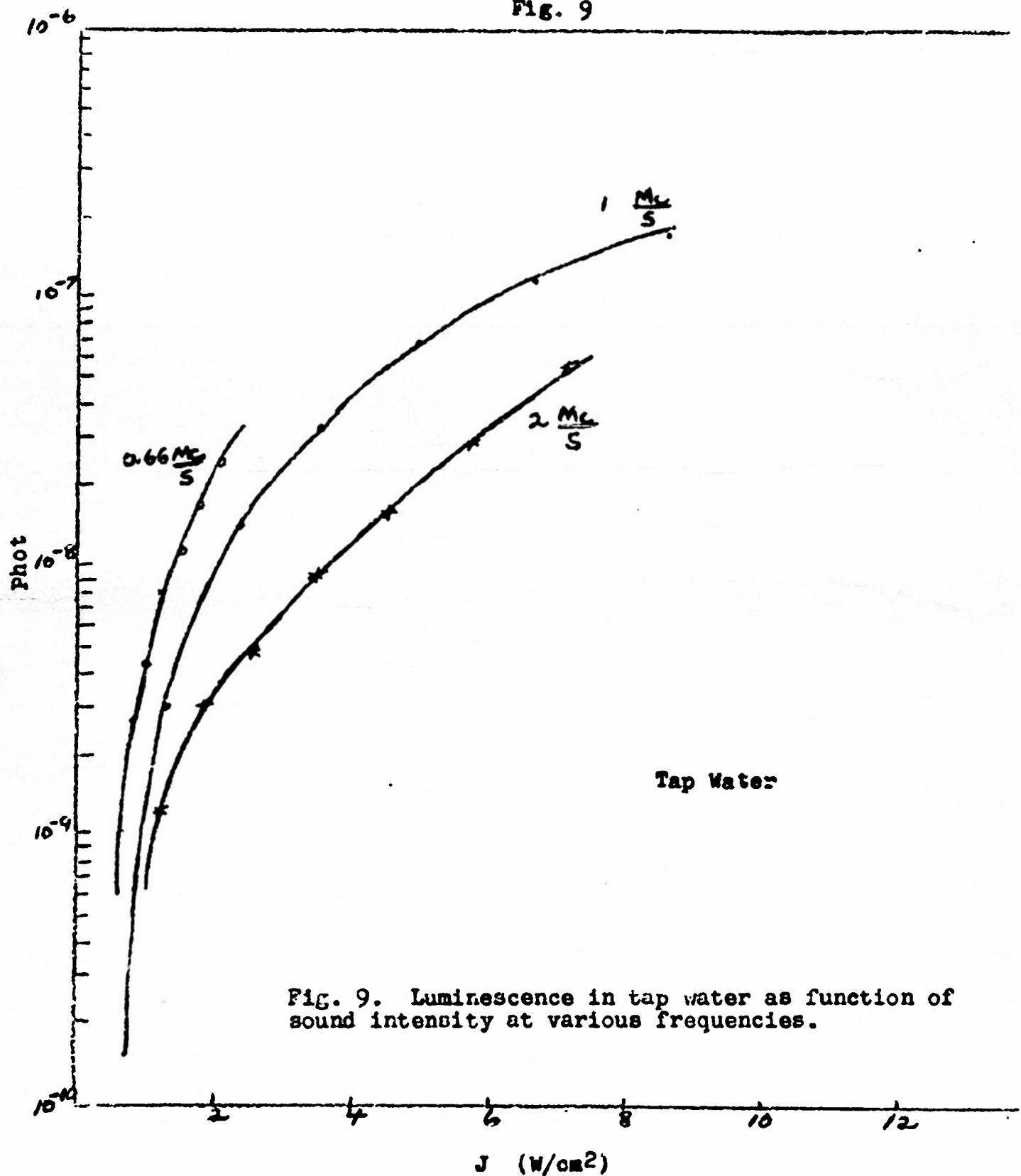
in liquids irradiated with ultrasonics it is only observed when
the sound intensity and gas content is sufficient to bring about
cavitation. In every case luminescence is observed only if cavi-
tation is observed. The cavitation threshold is the luminescence
threshold. In the water-carbon tetrachloride-hydrogen system even
though cavitation was observed there was no luminescence; in the
case of all the organic liquids observed except nitro-benzene
cavitation was observed but no luminescence. In these cases where
there was no observable luminescence there was also no observable
chemical reaction. In previously reported[6] observations qualitative
estimates of the intensity of luminescence were correlated with the
measured yield of chemical reaction. These observations were made
using various dissolved gases, e.g. argon, notrogen, oxygen, carbon
monoxide, sulfur hexafluoride and some of the freons. The quantita-
tive measurements of luminescence given in figure 6 were made on
systems which covered a reasonable range of chemical yield. These
measurements show a quantitative agreement between the intensity of
luminescence and the yield of chemical reaction. The intensity of
luminescence, and yield of free chlorine, and the observed cavita-
tion were all greatest for the water-carbon tetrachloride-argon
system even though other experiments to be reported elsewhere have
shown that the argon slightly increases the threshold of cavitation.
Thus it would seem that the luminescence, observed in water solutions,
always accompanied by cavitation, is actually chemiluminescence.

The luminescence observed in nitro-benzene is of a completely
different order of magnitude and thus it is doubtful if any chemical
reaction would be observable even if it occurred. It is entirely
possible that this luminescence could also be of chemical origin
either due to traces of water or other impurities in the nitrobenzene
or to a slight decomposition of the nitrobenzene itself. Chambers
has observed luminescence in the range of 1-10 Kc in a number of
liquids. His results do not agree with ours in theMc range, e.g.,
he finds stronger luminescence for nitro-benzene than for water.
Whether our weak nitrobenzene luminescence is of the same kind as
that observed by Chambers, and whether there are in general different
mechanisms in the different frequency ranges cannot be decided at
present.

Even though figure 9 would seem to indicate a frequency dependence
for the luminescence and the chemical yield figure 10 shows that the
threshold of cavitation is frequency dependent and if this dependence
is taken into account all of the results fall nicely on a single curve.

Fig. 10

Fig. 10. Luminescence in tap water at various frequencies as function of the ratio sound intensity/intensity at cavitation threshold.